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CERAMIC MEMBRANES FOR GAS SEPARATION AT HIGH TEMPERATURES

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ABSTRACT

Superior heat, wear, erosion, and corrosion resistance of ceramic materials have motivated the studies of processing-structure-performance interrelationships of ceramic membranes for high temperature gas separations. A literature review on pore transport mechanisms, physical structure of membranes, and module configuration of industrial membrane processes has been made to obtain a better understanding of membrane performance in gas separations. The research experience in decomposing polymer resins for ablative composites has stimulated a research interest in developing a dynamic model for membrane processes, incorporating a temperature effects on material and fluid properties. Brief summaries of the reviewed literature, permeability experiments, and process modeling are presented in this report.

INTRODUCTION

Ceramics are high-temperature materials which can be used at high temperature. Therefore, thermal stability has been considered as a great advantage of utilizing ceramic membranes for gas separation at high temperatures [1,2]. One of the most troublesome problems in research and development of ceramic membranes for high temperature applications is how to control the effects of the changes in thermostructural properties of the ceramic materials on membrane performance over a long service period [3-5]. As an initiation of a research program, this report emphasizes the membrane performance aspects. Thermal stability and process performance enter the discussion only as these topics pertain to membrane performance. A complete literature search was conducted and a technical bibliography was developed to support consolidation and assimilation of the knowledge acquired from the recent literature in membrane technology for gas separations. Another important objective of this report is to present a knowledge-based design basis for the membrane performance that combines the analytical analyses of transport phenomena, membrane structure, and mathematical modeling. Possible areas of application of the knowledge-based design basis include critical material properties development, gas separation system design, and membrane performance control.

Four commercially available module configurations for membrane processes are: flat sheet, tubular separator, spiral wound, and hollow fibers [6-8]. The module configuration has a significant effect on the fluid dynamics and thus, the performance of membrane processes. In addition to macro-form of membrane configuration, physical micro-structure also plays an important role in controlling the membrane performance [9-13]. Aim at investigating the thermal stability and high temperature performance of membrane gas separations, the present study

emphasizes the microstructural aspects, which in turn requires a thorough understanding of the transport mechanisms and process models for the membrane systems. This report will present a study in membrane microstructure, transport mechanisms, gas permeability experiments, and process modeling.

PHYSICAL STRUCTURE OF MEMBRANES

From a material engineering point of view, the performance efficiency of a membrane system for gas separations can be evaluated based on two factors: permeability and permselectivity. Mean permeability coefficient, p_a and specific permeability, k_a are two proportional constants used to represent the permeability of a membrane process; while separation factor, α , defined as $\alpha^{ab} = P_a/P_b$ is used to measure the permselectivity [14]. These parameters in turn will be determined by the microstructure of the membrane, fluid properties of the permeate streams, and the interaction between the fluid and membrane structure.

Basically there are two microstructural forms for membranes - porous and nonporous. Because transport rates through nonporous, dense films are inherently very low, they are not attractive for large-scale application in separation processes where productivity is of paramount concern. On the other hand, such films are ideal barriers for use in packaging foods and other items where certain components are to be kept in and others kept out. Membranes containing voids that are large in comparison with molecular dimensions are considered porous. The simplest pore geometry is that of parallel capillaries of uniform dimension extending throughout the thickness of the membrane.

In addition, membranes may have an asymmetry of physical structure characterized by a

gradation of pore sizes through the membrane or, in the extreme, a dense layer on top of a porous substructure. Furthermore, composite membranes may be tailored to meet specific demands, including both transport and mechanical properties desired for a specific application.

MECHANISMS OF PORE TRANSPORT

It is common to formulate a general rate equation for a transport process as

$$\text{Rate} = \frac{\text{Driving Force}}{\text{Resistance}} \quad (1)$$

Based on this formulation, the flux with which a gas permeates a membrane is given as

$$Q_s/A = P_s \left(- \frac{dp_s}{dx} \right) \quad (2)$$

where A is the membrane surface area, Q_s/A represents the steady-state volumetric flux, dp_s/dx is the pressure gradient, and P_s is the mean permeability coefficient. In a flow of fluid through porous media, depending on the permeation mechanism, different definitions for permeability coefficient, P_s , are used to describe the transport phenomena in a membrane process. Whether viscous flow or diffusive flow is present, the permeability coefficient, P_s , has to be determined experimentally.

If the pores are large compared to the mean free path, λ , viscous models can be used to describe transport within the pores. The mean permeability coefficient of Eq. (2) measured on the basis of the Darcy's law is the so-called hydraulic permeability; its dimensions are $M^{-1}L^3T^{-1}$. To separate the influence of the porous medium from that of the fluid, the specific permeability, k_s , of the porous medium is defined as:

$$P_a = \frac{k_a}{\mu} \text{ where } \mu \text{ is the fluid viscosity.} \quad (3)$$

The dimension of specific permeability is L^2 . In the oil industry, the unit of k is "darcy," with

$$1 \text{ darcy} = 9.87 \times 10^{-9} \text{ cm}^2. \quad (4)$$

For a porous membrane consisting of n uniform, cylindrical pores per unit area, the Hagen-

Poiseuille equation can apply directly to describe the permeation rate, and

$$Q/S = (n\pi r^4/8\mu)(\Delta P/l). \quad (5)$$

$$k = n\pi r^4/8 = \epsilon r^2/8 \quad (6)$$

where

$$\epsilon = n\pi r^2 \text{ is the porosity of the membrane} \quad (7)$$

When a porous membrane consists of a capillary bundle with noncircular cross section, the Darcy permeability defined by the Kozney-Carman equation is:

$$k = \frac{\epsilon^3}{k'(1-\epsilon)^2 S_o^2} \quad (8)$$

where S_o is surface area per unit particle volume.

The viscous flow governed by the Poiseuille and Kozeny-Carman equations is applicable in a limited range of pressure and temperatures such that the mean free path, λ , of fluid molecules is very small compared to the pore diameter, d . If the mean free path becomes comparable or larger than the pore size, the collision between gas molecules become much fewer than the collisions between gas molecules and the wall. This situation is known as "free-molecule diffusion" or "Knudsen flow." The rate equation for Knudsen flow in a long capillary tube is:

$$J_a = \frac{8\pi r^3}{3(2\pi RTM)^{1/2}} \frac{\Delta p}{l} \quad (9)$$

The steady-state equation for Fick's first law of diffusion is:

$$J_a = D_{k,a} \frac{\Delta C_a}{l} = \frac{D_{k,a}}{RT} \frac{\Delta p_i}{l} \quad (10)$$

Therefore, the Knudsen diffusion coefficient can be written in terms of model equations that involve the average pore radius, tortuosity, and porosity:

$$D_{k,a} = k \frac{r \epsilon}{\tau} (T/M)^{1/2} \quad (11)$$

Gas separation by means of permeation through a microporous membrane, where the pore diameter is smaller than the mean free path length, usually involves surface diffusion, in addition to Knudsen gas phase flows [15-17]. The degree of gas separation by surface diffusion flows is determined by the adsorption interaction of the respective gas-solid system. It was suggested that the gas permeability equation in microporous Vycor glass determined from the experimental data can be expressed as :

$$Q(MT)^{1/2} = A + BTe^{\Delta T} \quad (12)$$

The constant A represents the Knudsen gas-phase flow, while B and Δ the surface diffusion flow. The fraction of surface diffusion can be obtained by taking the ratio of the second term in Equation (12) to the value of $Q(MT)^{1/2}$.

Therefore, to obtain the fullest advantages of ceramic membranes for high-temperature gas separation, it is always desired to investigate the interrelationships of three dynamic material properties: thermal degradation, fluid dynamics, and gas permeability. Previous research efforts have concentrated on the experimental evaluation of the temperature effects on the mean permeability coefficient [18-20]. Recently, research on how gas permeability changes with increasing temperature due to thermal degradation of membrane microstructure has gained most emphasis [21-23].

GAS PERMEABILITY EXPERIMENTS

As discussed in the previous section, regardless of the nature of the transport mechanisms, the performance of a membrane can be characterized by measuring the permeability according to Eq. (2). The apparatus diagram of gas permeability experiments in this study is shown in Figure 1. Air was used as the planned, first series of experiments to study the feasibility of this apparatus in measuring the gas permeability of a ceramic membrane at room temperature.

A glass U-tube filled with distilled water was used as a manometer to measure the pressure drop as air permeates through the membrane disc. A commercial alumina Anodisc 47 Filter Membranes (0.2 μ pore diameter) was used for these first series of experiments. For a membrane with this large size of pore diameter, it is expected that the total molar flux of gas through the alumina membrane, mol/(sec-cm²), is the sum of the Knudsen and viscous flows:

$$Q_T = Q_k + Q_v \quad (13)$$

$$Q_k = \frac{\pi r_o^3 N \Delta p (2/(\pi R T M))^{1/2}}{3 \ell} \quad (14)$$

$$Q_v = \frac{\pi r_o^4 (P_1^2 - P_2^2)}{16 R T \ell \mu} \quad (15)$$

During these gas permeability experiments, one of the most troublesome problems was the reading of the pressure drop across the membranes. The readings were too small (0.1-0.4 cm) to have significant experiment results for the permeability measurement. Attempts to increase the permeation flow rate by changing the diameter of the permeation cell were discouraged, after some preliminary calculations showed that not much difference in pressure drop will be made by changing the disc diameters. Modifications of the apparatus during the last three months were not successful.

PROCESS MODELING

Membrane permeability and permselectivity, as described previously, are two factors used to evaluate the membrane performance. However, from a chemical engineering point of view, there are many processing parameters affecting the permeation operation. For a given gas mixture and membrane, these parameters include: the feed rate and composition, the pressure on the two sides of the membrane, the temperature, and the flow patterns of the permeated and unpermeated streams.

The development of membrane processes for high temperature gas separations requires a detailed knowledge of the relations among these parameters. The parameter analysis is more complicated in the case of a multicomponent, cascade process. Therefore, most of the theoretical analyses of membrane processes started with a single-stage gas permeation process [24-26]. Four flow patterns have been considered in developing analytical models for membrane performance. These are: countercurrent flow, cocurrent flow, cross-flow, and perfect mixing. Based on the extent of separation and membrane area requirements, countercurrent flow is the most efficient and perfect mixing is the least efficient one.

The permeate enrichment in a single-stage permeator is generally limited by the membrane selectivity and feed/permeate pressure ratio, recycling, multistage, or cascading configuration are usually required in order to achieve the higher performance/enrichment [25, 27-29]. Continuous membrane column (CMC) represents an innovative design for an efficient and simplified membrane-separation system. Analogous to a distillation column in which the gas mixture is fed to the column in between the stripping and the enriching sections, the more permeable gas gathers at the top of the enricher, and the less permeable gas gathers at the bottom of the stripper.

Similarly, to include diffusion effect in the plug-flow model numerical method is required to solve the problem.

Investigation of gas permeation through porous materials is also considered an important research area in preparing carbon-carbon composites from phenolic prepreps and in controlling the thermostructural behavior of decomposing, expanding polymer composites for rocket booster nozzles. As an ASEE/NASA summer faculty fellow in Marshall Space Flight Center (MSFC), Huntsville, AL, the author conducted solid-rocket-motor (SRM) nozzle project in 1992 and 1993 [30-32]. In a SRM nozzle, the generation of the internal gases from resin decomposition can be considered as a toughening mechanism, where pore-pressure stress strengthens the composite laminates. However, if the rate of internal gases generation is too high, a high pressure stress exceeding the fiber tensile strength or interlaminar shear strength is quickly developed and the material will be exploded and filed. On the other hand, if resin microcracking occurs during the SRM flight, internal gases will escape readily and the material will be degraded without an explosive blowout failure. These observation led to a conclusion that gas permeability plays an important role in the failure mechanisms of SRM nozzles.

Therefore, although my MSFC summer project did not directly involve the mathematical modeling of membrane processes, knowledge in permeation measurement and its effects on thermostructural behavior have provided me valuable information in initiating a study in analytically modeling of a membrane process for high temperature gas separations. Meanwhile, while working this MSFC summer project, I have done some literature research on the permeability study for the chemically charring polymer composites.

Research results in gas permeability pertinent to composite material have been reviewed

[33]. Due to the complex, changing porous structure of an ablative composite, the permeability of a decomposing, expanding composite involves many different transport mechanisms at different temperature regions. The rate of gases permeability is related to pressure build-up, microcracks, composite anisotropy, resin and voids infiltration rate, etc. For practical applications, Darcy's law in terms of flow resistance through porous medium has been used to define the permeability. Permeability constants of phenolic and epoxy composites based on Kozeny-Carman equation have been measured [33-35].

An important task in the present project was to study the feasibility of developing a gas permeation model, including the temperature effects of structure induced-pressure stress on membrane performance. This can be accomplished by studying the coupled phenomena of thermal degradation, fluid mechanics, gas permeability, and void formation and transport of the membrane system. However, the phenomena are coupled in such a complex way that a numerical analysis is needed.

SUMMARY AND RECOMMENDATIONS

Research in permeation processes and pore transport mechanisms have been reviewed. Interrelationships between three critical processing parameters of a membrane process - gas permeation, flow pattern, and membrane permeability have been described. Possible explanation of the difference in permeation performance, based on the process parameters of the permeation, mechanisms has been explored. An initial framework for modeling the temperature effects on the permeation performance was developed. It was concluded that numerical analysis is needed to study the coupled transport phenomena related to the temperature effects on the membrane performance.

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